Different Atomic bonding and their Nature.

Forces between Atoms in bonding structure:

Matter can exist in solid state only because there are forces of interaction acting between the atoms when they are brought close to each other, the forces of interaction between two atoms is two types — (i) attractive
(ii) repulsive..

The attractive forces between two atoms bring them close together until the individual electron clouds begin to overlap and a strong short range repulsive force arises to comply with pauli's Exclusion principle. At a certain separation, called the equilibrium separation, R_e, at which the attractive and repulsive forces are equal, the two atoms are in a stable situation and have minimum potential energy.

V = Decrease in potential energy due to attraction + Increase in potential energy due to repulsion.

$$\therefore \quad U = -\frac{A}{R^n} + \frac{B}{R^m} \quad \cdots (i)$$

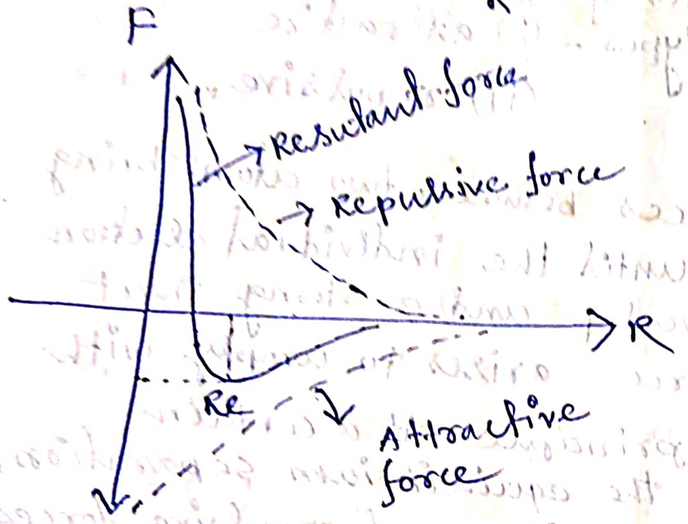
; where R is the separation.

A, B, m, n are constant depending on the nature of atoms.

∴ The force acting between two atoms as a function of R is given by,

$$F = -\frac{dV}{dR}$$

$$\therefore F = -\frac{nA}{R^{n+1}} + \frac{mB}{R^{m+1}} \quad (8)$$



At the equilibrium $R = Re$

$$F = \left(-\frac{dU}{dR}\right)_{R=Re}$$

$$\frac{nA}{Re^{n+1}} = \frac{mB}{Re^{m+1}}$$

$$\therefore Re = \left(\frac{mB}{nA}\right)^{\frac{1}{m-n}}$$

∴ From eqn (i),

$$U_e = -\frac{A}{Re^n}\left(1 - \frac{n}{m}\right)$$

The minimum energy U_e is negative. And a positive quantity $D = -U_e$ is the dissociation energy of molecules.

For V_e be minimum and negative at R_e.

$m > n$

Different charge distribution give rise to different types of bonding.

Different types of bonding —

i) Ionic Bonding
ii) Covalent Bonding
iii) metallic Bonding

— primary bondings have energy 0·1–10 eV/bond.

iv) Hydrogen Bonding
v) Van der walls Bonding

— secondary bonding have energy 0·01–0·5 eV/bond.

- Ionic Bonding and its characteristics:

i) The ionic bonding arises from the transfer of electron from a electropositive element to electronegative element, there by creating a positive and a negative ion.

ii) Ionic crystals has strong bond structure, high melting and boiling point.

iii) The substance formed by ionic bonding are generally insulators.

Bond Dissociation Energy of NaCl Molecule:

The ionisation process of a Na atom is represented by the reaction and Cl^- ion

$$Na(g) + I.P\,(energy) \longrightarrow Na^+(g) + Cl^-(g)$$

$$Cl(g) + \bar{e} \longrightarrow Cl^-(g) + E.A\,(energy)$$

The net amount of energy absorbed in the process of formation of positive sodium ion and a negative chlorine ion at infinity given by

$$\delta E = I.P - E.A$$

In the above reaction Na and Cl ions are separated at infinity. Now Na^+, Cl^- ions are bring to close together so that an ion pair is formed. when the Na^+, Cl^- ions are at equilibrium separation, a Stable NaCl molecule is fomed.

potential energy released at equilibrium

$$V_e = -\frac{e^2}{4\pi\epsilon_0 R_e}$$

The net energy relased is equal to bond dissociation energy is given by

$$D.E = V_e + I.P - E.A$$

Cohesive Energy of Ionic crystals:

The cohesive energy of ionic crystals is mainly due to electrostatic interaction. The cohesive energy (U) of a crystal containing oppositely charged ions with charge Z_1 and Z_2 is given by

$$U = -\frac{AZ_1Z_2e^2}{4\pi\epsilon_0 R} + B\exp\left(-\frac{R}{\rho}\right)$$

Here A is known as the Madelung constant and depends upon only the geometrical arrangement of ions in the crystals. B repulsion constant, ρ is the repulsion exponent.

For a NaCl crystals $(Z_1 = Z_2 = 1)$

$$\therefore U = -\frac{Ae^2}{4\pi\epsilon_0 R} + B\exp\left(-\frac{R}{\rho}\right)$$

$\therefore$ The total energy per kmol of the crystal is

$$U = N\left[-\frac{Ae^2}{4\pi\epsilon_0 R} + B\exp\left(-\frac{R}{\rho}\right)\right]$$

$$\left(\frac{dU}{dR}\right)_{R=R_e} = N\left[\frac{Ae^2}{4\pi\epsilon_0 R_e^2} - \frac{B}{\rho}\exp\left(-\frac{R_e}{\rho}\right)\right] = 0$$

$$\therefore \frac{B}{\rho}\exp\left(-\frac{R_e}{\rho}\right) = NAe^2/4\pi\epsilon_0 R_e^2$$

$\therefore$ potential energy at equilibrium separation is given by,

$$U_e = -\frac{Ae^2N}{4\pi\epsilon_0 R_e}\left[1 - \frac{\rho}{R_e}\right]$$

the ratio of ρ/R_e is found to lie between 0.09 to 0.12. This means repulsive force is short rangle.

Calculate the Madelung constant for an infinite linear chain of ions of alternating unit charge at separation R_e

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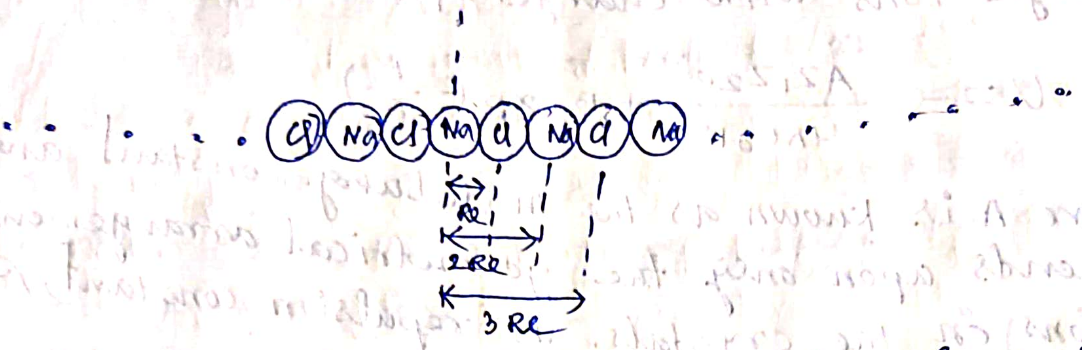


fig: one Dimensional NaCl crystal.

Here R_e be the separation between Na^+ and Cl^- ions at equilibrium.

Madelung constant

$$A = 2\left(1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \dots\right)$$

$$\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \dots$$

$\therefore \; A = 2\ln 2$

Covalent Bonding:

i) The bonding arises from shearing of one or more electrons by the atoms is known as covalent Bonding.

ii) Covalent crystals are very hard since the bond is very strong.

Ionicity of a Covalent bond A-B:

Pauling expressed the ionicity of a covalent bond A-B in terms of the difference between the electronegativities of these two atoms,

$$f_i = 1 - \exp\left\{ \frac{(X_A - X_B)^2}{4} \right\}$$

f_i is the fractional ionic character.

X_A and X_B are pauling electronegativity of element A and B.

In crystals this expression is modified to account the fact that an atom forms more than one bond.

For $A^N B^{8-N}$ crystals,

$$f_i^c = 1 - \left(\frac{N}{M}\right) + \left(\frac{N f_i}{M}\right)$$

M = number of neighbours.

Mettalic Band:

In metals the electrons in the outermost orbit are loosely bound and are called free electrons. one and more electrons of the parent element detached by the attraction of adjacent atomic core. The positively charge atoms are known as Kernal. Thus the metal crystals are pictured as the arrangement of positive ions immersed in the sea of free electron. The motion of free electron is such that they are simultaneously near two or more Kernals and bind them together. The bond thus formed between the metal atoms are known as mettalic Bond.

- Metallic crystal have high themal and electrical conductivity because the presence of free electron.

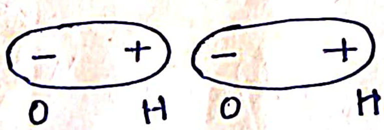
Van Der Waal's Bonding:

The atoms of inert gases have no free/valence electron as their outermost orbit are completely filled. They are not capable of forming any types of Bonding. The organic molecules like CH_4 have configuration like inert gas.

However, these molecules condense to liquid or solid by decreasing temperature.

To explain this vander waal suggested some type of attractive force between the molecules of inert gas. The weak attractive force is Vander wall force. The vander wall force between two molecules at separation r is proportional to $\frac{1}{r^7}$, so the van Der wall force is short range force.

example: Bonding between H_2O molecules due to permanent ~~electric moment~~ Dipole moment



Hydrogen Bonding:

A speacially strong van Der wall force acting between two molecules contain hydrogen atoms. Hydrogen atoms has oney one electron in the outer orbital by loses some to the other constituent atom and ~~the~~ hydrogen atom bind with the electronegative atoms. The H^+ ion can have any two negative ions because its radius (10^{-15} m) thousands of time smaller than the radius of the other ion.